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REPORT NO. 3396 (SEMIANNUAL)
PERIOD COVERED: 1 OCTOBER 1966 - 31 MARCH 1967

RESEARCH IN FLUORO-NITRO
COMPOUNDS (U)

A REPORT ON WORK SPONSORED BY

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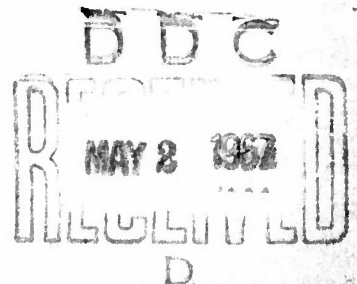
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APRIL 1967

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April 1967

Report No. 3396
(Semiannual)

RESEARCH IN FLUORO-NITRO COMPOUNDS (U)

By

K. Baum, V. Grakauskas, H. F. Shuey

Analytical Support: K. Inouye, L. A. Maucieri

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ABSTRACT

The reaction of 2-phenylazo-2-nitropropane with difluoramine and fuming sulfuric acid gave 2-phenylazo-2-difluoraminopropane, benzene, acetone, 2,2-bis-(difluoramino)propane and O-(2-difluoraminopropyl)acetone oxime.

The nitration of 2-phenylazo-2-difluoraminopropane has not yielded 2-nitro-2-difluoraminopropane, although 2-phenylazo-2-nitropropane gave 2,2-dinitropropane. No product of interest resulted from the reactions of difluoramine with ethyl nitrodiazoacetate, ethyl 2-butylnitronate, 1-diazo-2-heptanone, 2-nitropropene, diphenyliodine tosylate, and 1-iodo-1-nitrocyclohexane.

A new NF compound was found in the reaction of 1-nitro-1-nitrosocyclohexane with difluoramine and 100% sulfuric acid.

The reaction of 2-bromo-2,4,4-trinitropentane with difluoramine and fuming sulfuric acid resulted in extensive replacement of nitro groups.

The reaction of 3,3-bis(difluoramino)pentane with fluosulfonic acid gave 3-pentanone and difluoramine.

Fluoroammonium perchlorate underwent no decomposition in 4 months at ambient temperature in a Teflon container.

An approximate value of the heat of formation of SAP, -67.6 kcal/mole, was determined by rotating bomb calorimetry.

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CONTRACT FULFILLMENT STATEMENT

This semiannual technical report is submitted in partial fulfillment of the contract and covers the period from 1 October 1966 to 31 March 1967.

AEROJET-GENERAL CORPORATION



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I. INTRODUCTION

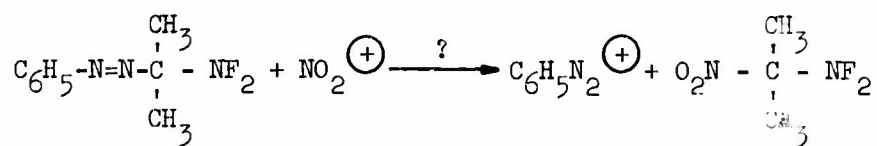
The objective of this program is to develop new methods of preparing high-energy compounds of interest for military applications.

II. REACTIONS OF DIFLUORAMINE (K. Baum and H. F. Shuey)

A. DISCUSSION

Compounds having geminal bis-difluoramino groups and nitro groups in the same molecule separated by two methylene groups are prepared readily from the corresponding nitroketones.* However, no general method is available for the synthesis of higher energy compounds of this type with fewer intervening methylene groups. Another type of difluoramino-nitro compound that would be of particular interest is that with difluoramino and nitro groups on the same carbon atom. Besides providing an oxygen source for propellant combustion, the nitro groups might alter the sensitivity characteristics of the difluoramino groups.

In the report for the preceding period,** the reaction of 2-phenylazo-2-nitropropane with difluoramine was studied with the objective of preparing 2-nitro-2-difluoramino-propane. The only product isolated other than starting material was 2-phenylazo-2-difluoraminopropane; the nitro group rather than the phenylazo group was replaced by difluoramine. Work was continued on this reaction, since 2-nitro-2-difluoraminopropane might alternatively be obtained by the nitrolysis of 2-phenylazo-2-difluoraminopropane.



* Aerojet-General Report No. 0235-01-13, March 1962 (Confidential).

** Aerojet-General Report No. 3299, October 1966, p. 10 (Confidential).

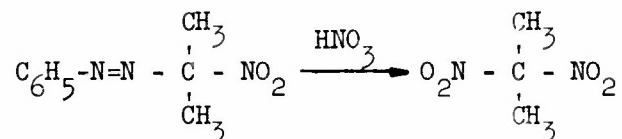
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II Reactions of Difluoramine, A (cont.)

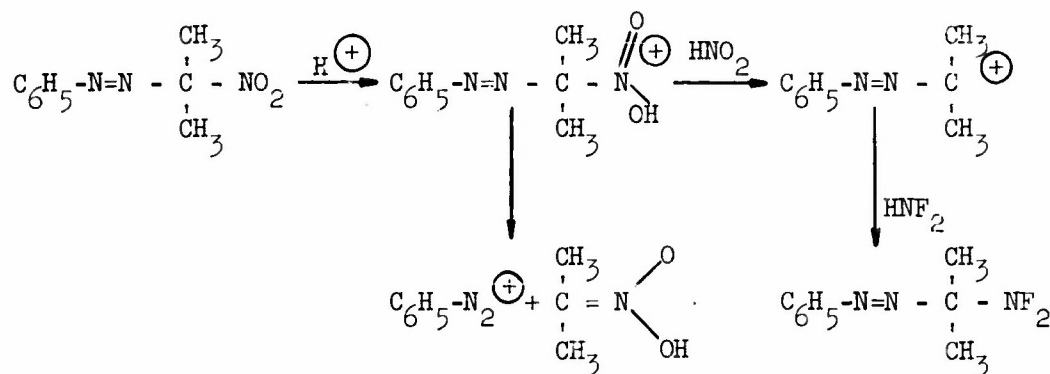
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The feasibility of this approach was demonstrated by the nitration of the more readily available starting material, 2-phenylazo-2-nitropropane. No reaction took place between this compound and N_2O_4 in methylene chloride, whereas a mixture of ammonium nitrate and nitric acid gave a complex tarry product. However, anhydrous nitric acid at 0 to 25°C gave a 37% yield of 2,2-dinitropropane:



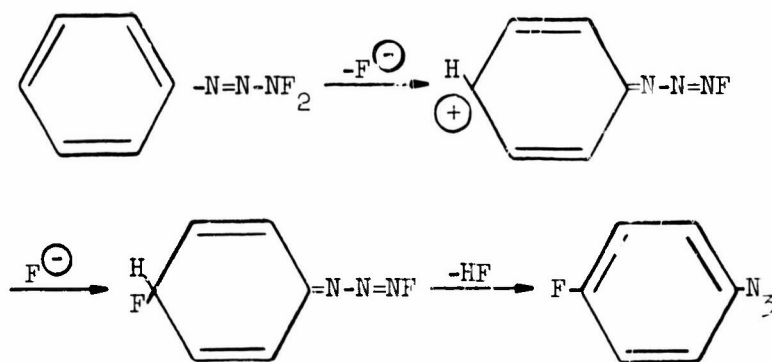
The reaction of 2-phenylazo-2-nitropropane with difluoramine, catalyzed by sulfuric acid, was scaled up and the reaction time was extended in order that sufficient 2-phenylazo-2-difluoraminopropane might be prepared for nitration studies; a 17% yield of analytically pure material was thus isolated (the previously prepared material was somewhat impure). Other products of this reaction were benzene, acetone, acetone oxime, 2,2-bis(difluoramino)propane, phenyl azide, and O-(2-difluoraminopropyl) acetone oxime. The latter compound was identified by elemental analysis, NMR, and infrared spectra (Figure 1).

The observed products appear to arise from the initial protonation of a nitro oxygen of 2-phenylazo-2-nitropropane. The protonated species might then undergo two types of cleavage: loss of nitrous acid to give a secondary carbonium ion; and loss of benzenediazonium ion, leaving aci-2-nitropropane. Alkylation of difluoramine by the secondary carbonium ion would give 2-phenylazo-2-difluoraminopropane.



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Benzene, *o*-fluorophenyl azide and *p*-fluorophenyl azide have been shown to be products of the reaction of benzenediazonium ion and difluoramine, under mildly basic conditions.* The formation of benzene was rationalized on the basis of reduction of diazonium ion by difluoramine, and the formation of the fluoroazide was ascribed to coupling of the diazonium ion to difluoramine with subsequent rearrangement of the triazene:

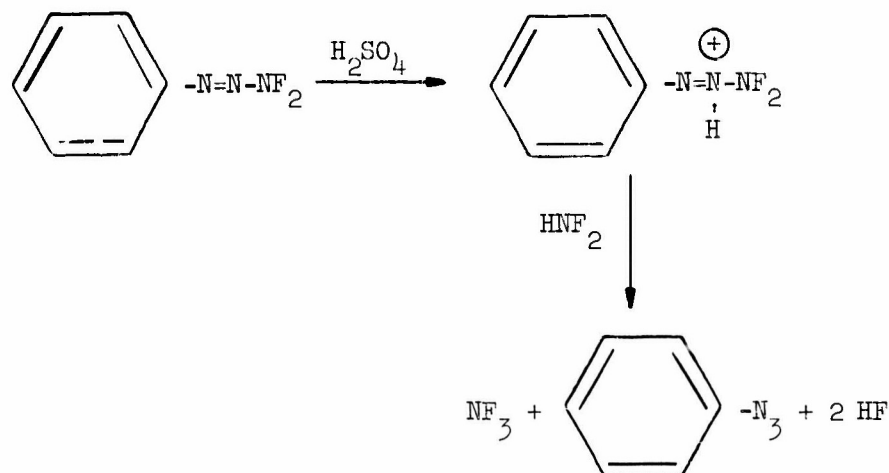


In the present work, in which strongly acidic reaction conditions were used, unsubstituted phenyl azide was formed rather than the fluoro derivatives. This result can be explained on the basis that the initially formed triazene would be protonated by sulfuric acid. Loss of fluoride is then inhibited because it leads to an unstable, doubly-charged cation. Phenyl azide will be formed if fluorine is lost in an electrophilic fluorination reaction (e.g., converting difluoramine, the most abundant substrate available, to trifluoramine).

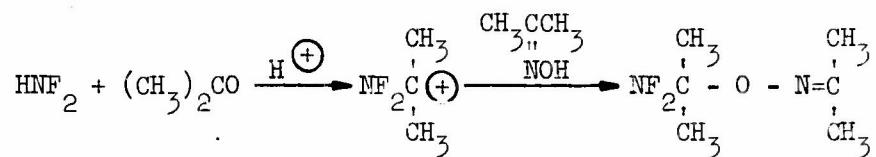
The fact that phenyl azide is formed from benzenediazonium ion and difluoramine in sulfuric acid was confirmed in a control experiment. The addition of benzenediazonium fluoborate to a mixture of concentrated sulfuric acid, and refluxing difluoramine gave phenyl azide and no fluorine-containing derivatives.

* Aerojet-General Report No. 0235-01-25/26, September 1966 (Confidential).

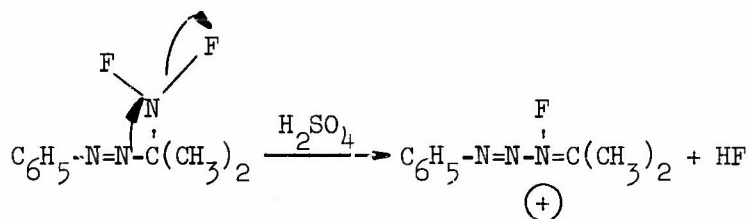
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The product, acetone, from the reaction of 2-phenylazo-2-nitropropane and difluoramine could be formed by the hydration of the 2-phenylazo-2-propyl cation, or by the Nef reaction of aci-2-nitropropane. The source of the acetone oxime, on the other hand, is less clear. The compound might be formed by the reduction of the aci-2-nitropropane by difluoramine. The O-(2-difluoraminopropyl) acetone oxime could be formed from acetone oxime, difluoramine and acetone.



To gain additional information about the side reactions, a solution of pure 2-phenylazo-2-difluoraminopropane in sulfuric acid was prepared for NMR studies. The solution was intensely green colored. The F^{19} spectrum consisted of two broadened peaks of about equal intensity at -117.0 and -110.5 ppm from trifluoroacetic acid. The former is at the same position as that of a solution of HF in sulfuric acid. The proton spectrum consisted of a multiplet in the aromatic region at 8.3 to 9.9 δ and 2.2 δ . These spectra suggest that ionization of fluoride from the difluoramino group took place, with migration of the phenylazo group.



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II Reactions of Difluoramine, A (cont.)

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This ion might account for the side products in the synthesis of 2-phenylazo-2-difluoraminopropane, since hydrolysis during work-up could give benzenediazonium ion and acetone oxime derivatives.

Attempts were made to nitrate 2-phenylazo-2-difluoraminopropane with 100% nitric acid and with nitronium fluoborate. Degradation of the starting material took place, and 2-difluoramino-2-nitropropane was not isolated.

The possibility of preparing an α -difluoramino nitro compound from an α -iodonitro compound was studied briefly. The syntheses of crude 2-iodo-2-nitropropane and 2-iodo-2-nitrobutane have been reported, but the compounds were too unstable for distillation.* Using the same method, 1-iodo-1-nitrocyclohexane was prepared, which gave analytically pure material by low-temperature crystallization. This compound did not react with liquid difluoramine at its boiling point. In the presence of sulfuric acid, no product extractable from water was formed. This iodo compound was also treated with tetrafluorohydrazine, but no reaction took place at 80°C and, at 120°C, the mixture exploded.

The reaction of difluoramine with 2-nitropropene could be expected to result in Michael addition, as was found with other conjugated olefins such as acrylates and vinyl ketones. It was found, however, that no reaction took place between these reagents when no catalyst was used or when the boron trifluoride complex of phosphoric acid was added. The use of concentrated sulfuric acid resulted in the decomposition of the 2-nitropropene. Isopropyl N-fluorocarbamate also failed to add to 2-nitropropene in the presence of pyridine. It appears that the addition is reversible with the equilibrium shifted toward starting materials because of the acidity of the hydrogens adjacent to the nitro group.

Another possible route to α -nitro difluoramino compounds that was investigated briefly is the reaction of α -diazonitro compounds with difluoramine. It was shown previously that the reaction of ethyl diazoacetate with difluoramine in the presence of sulfuric acid gave ethyl difluoraminoacetate.** Ethyl azo-nitroacetate, contaminated by ethyl nitroacetate, was prepared by the reaction

*L. W. Seigle and H. B. Haas, J. Org. Chem., **5**, 100 (1940).

**Aerojet-General Report No. 3299, October 1966, p. 10 (Confidential).

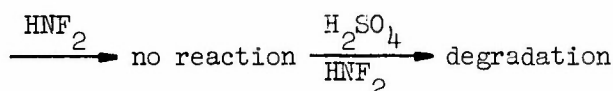
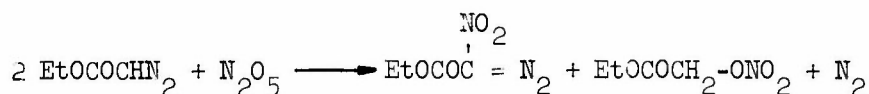
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II Reactions of Difluoramine, A (cont.)

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of nitrogen pentoxide with ethyl diazoacetate.* No reaction took place with difluoramine in the absence of catalysts, and with the addition of sulfuric acid, no fluorine-containing products were found.



Some additional work was done on the reaction of pseudonitroles with difluoramine. It was shown previously that gem-difluoramines were formed in the presence of fuming sulfuric acid and that fluoroazoxy-nitro compounds were formed in the presence of the boron trifluoride complex of phosphoric acid.** It appeared the nitro-difluoramino compounds should be formed with a catalyst of intermediate activity. Trifluoroacetic acid, concentrated sulfuric acid, and 100% sulfuric acid have now been investigated for the reaction of nitronitrosocyclohexane and difluoramine. With trifluoroacetic acid and with concentrated sulfuric acid, no reaction took place; the nitroso compound was insoluble in the reagent. When 100% sulfuric acid was used as the catalyst and the nitroso compound was dissolved in methylene chloride, a new compound was formed, with an F^{19} NMR signal at -23.4ϕ . The amount of this material that was formed was not sufficient for complete characterization, but this reaction will be repeated.

The reaction of ethyl 2-propylnitronate with difluoramine was also attempted. When no catalyst was used no fluorine-containing product was formed. When concentrated sulfuric acid was used, the product gave very weak F^{19} signals at -28.0ϕ , -24.4ϕ , and -19.1ϕ .

Attempts to isolate 2,2,4-trinitro-4-halohexanes by the halogenation of 2,2,4-trinitrohexane have been unsuccessful.*** 2-Bromo-2,4,4-trinitropentane

* U. Schollkopf and H. Schafer, Ang. Chem. (Int. ed.) 4, 358 (1965).

** Aerojet-General Report No. 2945, October 1964, p. 5 (Confidential).

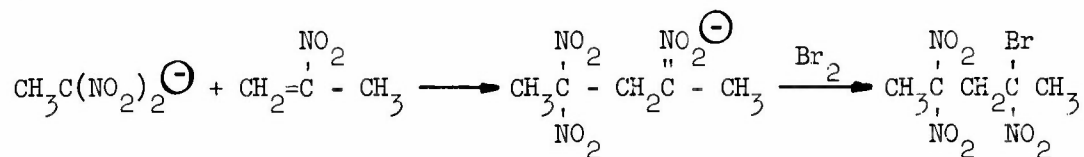
*** Aerojet-General Report No. 3299, October 1966, p. 8 (Confidential).

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II Reactions of Difluoramine, A (cont.)

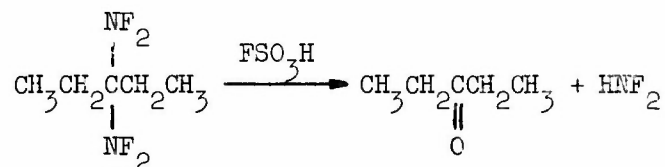
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has now been synthesized by the addition of the sodium salt of dinitroethane to 2-nitropropene, followed immediately by the bromination of the resulting nitronate salt:



One attempt was made to react 2-bromo-2,4,4-trinitropentane with difluoramine in the presence of fuming sulfuric acid. A product was obtained with elemental analysis corresponding to $\text{C}_5\text{H}_7\text{N}_2\text{F}_3\text{O}$. Area ratios in the proton nmr spectrum, however, indicated that the material was not a pure compound. Chromatographic purification of the material is in progress. It is evident, nevertheless, that extensive replacement of nitro groups took place. A considerable amount of starting material was recovered in the reaction, so it appears that the gem-dinitro groups are made reactive by cyclic participation with the initially formed carbonium ion.

Gem-difluoramines have been shown to hydrolyze reversibly in sulfuric acid to give ketones and difluoramine.* A stronger acid, fluosulfonic acid, was treated with 3,3-bis(difluoramino)pentane, in the hope that a more useful reaction would take place. However, the nmr spectra of the resulting solution showed that 3-pentanone and difluoramine were formed.



B. EXPERIMENTAL

1. Reaction of 2-Phenylazo-2-Nitropropane with Difluoramine

Freshly prepared 2-phenylazo-2-nitropropane (19.1 g, 0.102 moles) was added to a mixture of 30 ml of 20% fuming sulfuric acid and 27 g of difluoramine. The reaction mixture was maintained at the reflux temperature of difluoramine for 2.5 hours, and was then drained onto 300 ml of crushed ice. The product

* Aerojet-General Report No. 0235-01-22, May 1965, p. 5 (Confidential).

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II Reactions of Difluoramino, B (cont.)

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was extracted with three 100-ml portions of methylene chloride, which were then combined, dried over sodium sulfate and distilled through a 10-in. Holzmänn column. After the solvent was removed, vacuum distillation gave 3.40 g (0.0171 moles, 17% yield) of 2-phenylazo-2-difluoramino-propane, b.p. 65-67°/0.2 to 0.3 mm.

Anal. Calc'd for $C_9H_{11}N_3F_2$: C, 54.3; H, 5.54; N, 21.1; F, 19.1.
Found: C, 54.19; H, 5.27; N, 20.94; F, 19.4.

The infrared spectrum of the material was identical with that reported previously,* with the exception that the small peak at 6.3 μ was reduced to half the intensity.

The dry-ice trap used in this distillation was found to contain 0.5 g of a solid that melted near room temperature, characterized as O-(2-difluoramino-2-propyl acetone oxime, 3% yield.

Anal. Calc'd for $C_6H_{12}N_2F_2O$: C, 43.37; H, 7.24; N, 16.87; F, 22.89
Found: C, 43.73; H, 7.29; N, 16.89; F, 22.30

The F^{19} nmr spectrum (without solvent) consisted of a broadened singlet at -21.9 ϕ . The proton spectrum contained a symmetrical triplet ($J_{HF} = 2.5$ cps) at 1.55 δ , assigned to the methyls adjacent to the NF_2 , and a broadened singlet at 1.84 δ . The areas of the two signals were essentially equal. The infrared spectrum is shown in Figure 1.

The infrared spectrum of the above recovered solvent showed that it contained a small amount of 2,2-bis(difluoramino)propane.**

The aqueous solution remaining from the above extraction was neutralized by the addition of solid sodium carbonate with stirring and ice-bath cooling. Water (300 ml) was added, and the product was extracted with three 100-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and was distilled. The recovered solvent was shown to contain a small amount of acetone by its infrared spectrum. The residue was heated to 70° at 0.2 mm to give 1.0 g of material which collected in the -80° trap.

* Aerojet-General Report No. 3299, October 1966, Figure 1 (Confidential).

** Aerojet-General Report No. 0235-01-10, April 1961 (Confidential).

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The infrared spectrum of the material showed mainly peaks characteristic of phenyl azide and acetone oxime. The proton nmr spectrum confirmed that these compounds comprised 43.5 and 27.5 mole%, respectively, of the sample, with the remainder consisting of benzene (12%), water (8%), acetone (4%), methylene chloride (3%), and O-(2-difluoramino-propyl) acetone oxime (2.5%).

2. Nitration of 2-Phenylazo-2-Nitropropane

To 200 ml of anhydrous nitric acid at 0°C, 10 g (0.0518 moles) of 2-phenylazo-2-nitropropane was added dropwise with stirring over 5 min. The solution was allowed to warm to room temperature and then was added to 1 liter of crushed ice. The product was extracted with three 100-ml portions of methylene chloride.

The methylene chloride solution was dried over sodium sulfate and the solvent was removed at aspirator pressure using a rotary evaporator. The residue, 4.4 g, was vacuum distilled to give 3.52 g of liquid, b.p. 80°/11 mm. The infrared spectrum of this liquid indicated 2,2-dinitropropane contaminated by a nitrate ester impurity. This liquid was added to 10 ml of concentrated sulfuric acid and extracted with 25 ml of methylene chloride. Removal of the solvent left 2.55 g (0.019 moles, 37% yield) of 2,2-dinitropropane, m.p. 43 to 48; its infrared spectrum was identical to that of an authentic sample.

The reaction was repeated using a mixture of 100 g of nitric acid and 128 g of ammonium nitrate instead of anhydrous nitric acid as the nitrating agent. A black solution was formed from which no 2,2-dinitropropane could be isolated.

When a solution of 5 ml of N_2O_4 in 40 ml of methylene chloride was used as the nitrating agent, starting material was recovered quantitatively after a one-hour reaction period at ambient temperature.

3. 1-Iodo-1-Nitrocyclohexane

Nitrocyclohexane (3.87 g, 30 mmoles) was dissolved in 6.6 ml of 5 N sodium hydroxide with agitation and intermittent heating with hot tap water. This solution was cooled to room temperature and was added dropwise to a solution of 7.62 g (30 mmoles) of iodine and 4.98 g (30 mmoles) of potassium iodide in 30 ml of water. The mixture was stirred for 10 min; then, a dark

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heavy oil that separated was extracted into 40 ml of pentane. The pentane solution was cooled to -80°C to crystallize the product, and the pentane was decanted off. The product, which melted below room temperature, was recrystallized twice in this manner to give an amber colored oil. This oil was dried at 20 mm Hg for 15 min to give 5.4 g (21.2 mmoles, 64% yield) of 1-iodo-1-nitrocyclohexane.

Anal. Calc'd for $\text{C}_6\text{H}_{10}\text{NO}_2\text{I}$: C, 28.3; H, 3.93; N, 5.50.

Found: C, 28.19; H, 3.82; N, 5.32.

4. Reaction of 1-Diazo-2-heptanone with Difluoramine

1-Diazo-2-heptanone (2.0 g) was added dropwise, over 40 min, to a mixture of 5 ml of 20% fuming sulfuric acid and 4.5 g of refluxing difluoramine. The mixture was stirred for 3 hours and was then drained onto 100 ml of ice. The product was extracted with three 15-ml portions of methylene chloride, and the combined solutions were dried over sodium sulfate and concentrated to 5 ml by distillation through a Holzmman column. The F^{19} nmr spectrum of the solution gave no signal. The infrared spectrum showed that the diazo group ($4.78\ \mu$) was gone but carbonyl absorption ($5.81\ \mu$) was still present.

5. Reaction of Diphenyliodine Toluenesulfonate with Difluoramine

A mixture of 2 g of diphenyliodine toluenesulfonate* and 4.5 g of difluoramine was allowed to reflux for 3 hours. A clear solution was formed. Removal of the difluoramine left unchanged starting material.

6. Reaction of Ethyl-2-butyl-nitronate with Difluoramine

Difluoramine (4.5 g) was condensed onto 2 g of ethyl-2-butyl-nitronate** at -80° , and the mixture was allowed to reflux under a -80° condenser for 1 hour and 40 min. The difluoramine was then flushed from the system and the residue was dissolved in 6 ml of methylene chloride. The F^{19} nmr spectrum of the solution showed that it contained only a trace of fluorine, although the infrared spectrum showed that the starting material was no longer present. No further attempt was made to identify the product.

* N. Kornblum and H. J. Taylor, J. Org. Chem., **28**, 1424 (1963).

** N. Kornblum and R. A. Brown, J. Am. Chem. Soc., **86**, 2681 (1964).

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7. Reaction of Ethyl Diazonitroacetate with Difluoramine

A solution of 2 g of an equimolar mixture of ethyl diazonitroacetate and ethyl nitroacetate* in 20 ml of methylene chloride was added dropwise with stirring to a mixture of 7 ml of concentrated sulfuric acid and 4.5 g of refluxing difluoramine. The mixture was stirred for 75 min after the addition was complete, and was then drained onto 100 ml of ice. The methylene chloride solution was dried and was concentrated to 5 ml by distillation of the solvent. The F^{19} nmr spectrum of the solution showed no signal.

No reaction took place when 2 g of the undiluted starting material was treated with 4.5 g of refluxing difluoramine for 2.5 hours.

8. 2-Bromo-2,4,4-trinitropentane

2-Nitropropene (9.6 g, 0.11 mole) was added to a solution of 4.4 g (0.11 mole) of sodium hydroxide and 7.4 g (0.10 mole) of 1,1-dinitroethane in 50 ml of water at 7°C. A yellow salt precipitated immediately. Bromine (17.6 g, 0.11 mole) was added dropwise, with stirring, to this slurry; the slurry was kept below 10°C by external cooling. A viscous oil precipitated, and was separated from the aqueous layer and was dissolved in 75 ml of methylene chloride. The solution was washed with four 30-ml portions of water, and was dried over sodium sulfate. Removal of the solvent with a rotary evaporator gave 20.4 g of greenish-brown oil. Vacuum distillation gave 3.3 g of a dark oil, b.p. 25°/0-15 mm; 1 g of an intermediate fraction, 5.4 g of oil, b.p. 104-5°/0.15 mm; and an additional 0.7 g of dark oil as the pot temperature was raised. The latter three fractions solidified on standing; they were combined and recrystallized from ethanol to yield 4.4 g (0.0154 moles, 15.4% yield) of 2-bromo-2,4,4-trinitropentane, a white solid, m.p. 54°C.

Anal. Calc'd for $C_5H_8N_3O_6Br$: C, 20.99; H, 2.80; N, 14.69.

Found: C, 20.67; H, 2.67; N, 14.36.

The nmr spectrum of 2-bromo-2,4,4-trinitropentane consisted of a slightly broadened singlet at 4.06 δ (CH_2), a sharp singlet at 2.29 δ [$CH_3C-(NO_2)_2$] and a slightly broadened singlet at 2.12 δ (CH_3CNO_2Br).

*U. Schollkopf and H. Schafer, Ang. Chem. (Int. ed.) 4, 358 (1965).

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9. Reaction of 2-Bromo-2,4,4-trinitropentane with Difluoramine

A solution of 4.2 g (0.0147 moles) of 2-bromo-2,4,4-trinitropentane in 4 ml of methylene chloride was added, with stirring, to a mixture of 14 ml of 20% fuming sulfuric acid and 27 g of refluxing difluoramine in a (nitrogen atmosphere) glass reactor fitted with glass and Teflon needle valves. The reactor valves were closed and the mixture was stirred at room temperature for 3 hours. The mixture was drained onto 200 ml of ice, and the product was extracted with four 25-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate, and the solvent was removed by means of a 10-in. Holzmann column. A product (0.2 g) was isolated in a dry-ice-cooled receiver by heating the residue at 55°C/250 mm; another 0.2 g fraction was obtained by gradually raising the temperature to 90°, and reducing the pressure to 0.2 mm. Subsequently, 1.6 g of 2-bromo-2,4,4-trinitropentane was recovered, b.p. 93 to 94°/0.15 mm. From a dry-ice trap in series with the apparatus used in the latter distillation, approximately 1 ml of liquid was recovered with infrared absorption identical to that of the other two low boiling fractions.

The infrared spectrum is shown in Figure 2.

Anal. Calc'd for $C_5H_7ON_2F_3$: C, 35.70; H, 4.17; N, 16.66, F, 33.9.

Found for the second fraction: C, 34.31; H, 4.14; N, 16.92; F, 32.3.

The proton nmr spectrum consisted of a broadened signal at 5.81 δ (area, 24), a broadened symmetrical signal at 2.93 δ (area 18), a superposition of two sharp singlets at 2.35 δ (area 78), a sharp singlet at 2.20 δ (area 76), and a symmetrical quintet ($J = 2.2$ cps) at 1.76 δ (area 56).

10. Reaction of 3,3-bis-Difluoraminopentane with Fluosulfonic Acid

To 1 ml of fluosulfonic acid at -78°, 0.2 ml of 3,3-bis(difluoroamino)-pentane* was added. The solution was warmed slowly to ambient temperature. The F^{19} nmr spectrum contained singlets at -32 ϕ and -54.6 with relative areas of 20.1. The proton spectrum (a triplet at 1.35 δ and a quartet at 3.30 δ) was identical with that of a solution of 3-pentanone in fluosulfonic acid.

* Aerojet-General Report No. 0235-01-10, April 1961, p. 11 (Confidential).

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III. FLUORAMMONIUM PERCHLORATE (V. Grakauskas)

Two more 70-g batches of fluorammonium perchlorate (SAP) were synthesized by the previously described procedure,* and the material was shipped to other investigators for propellant evaluation.

A 25-g sample of SAP was stored in a Teflon container at room temperature in a dry box for four months. The material was analyzed periodically and its elemental and differential thermal analyses showed that no decomposition occurred on storage.

The compound was found to possess unusual solubility characteristics compared to other inorganic perchlorates in that it is very soluble in organic solvents, such as aliphatic esters and nitriles. Solutions of SAP might thus be useful liquid monopropellants, particularly if energetic solvents are used.

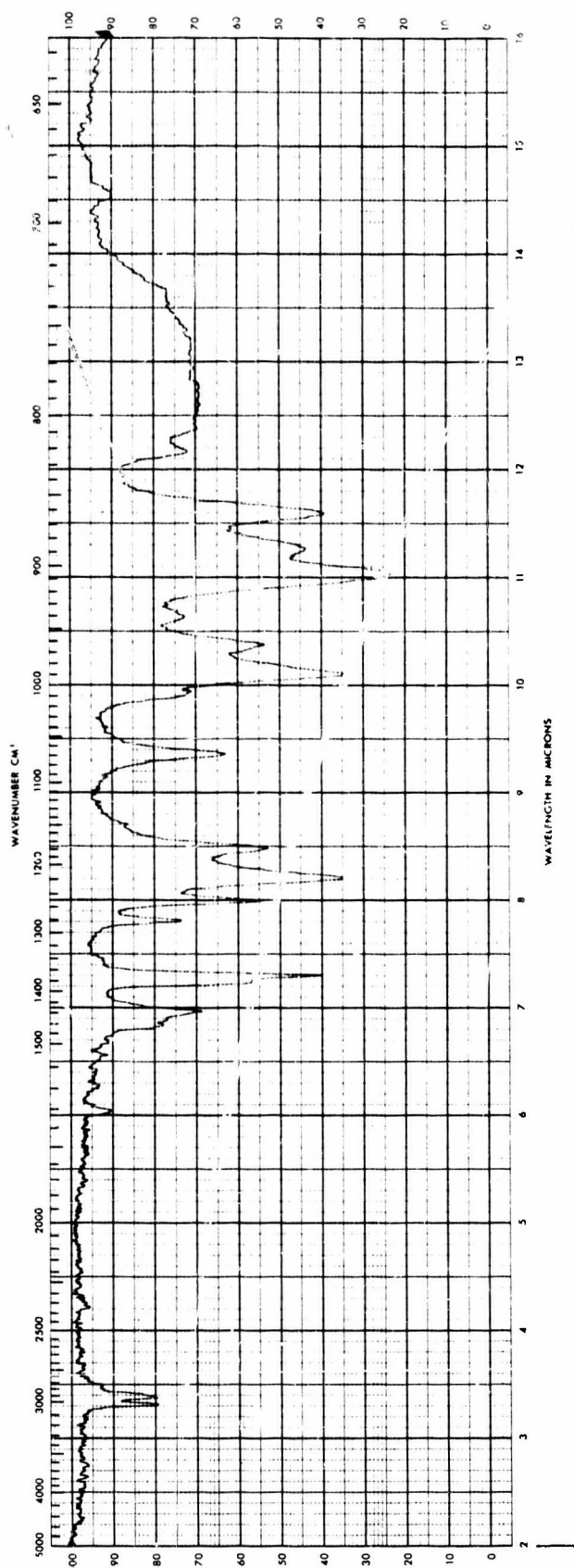
Thermochemical studies of SAP, conducted at the Aerojet facilities at Sacramento are presented in the Appendix.

*Aerojet-General Report No. 3299 (Annual Summary), October 1966, p. 14 (Confidential).

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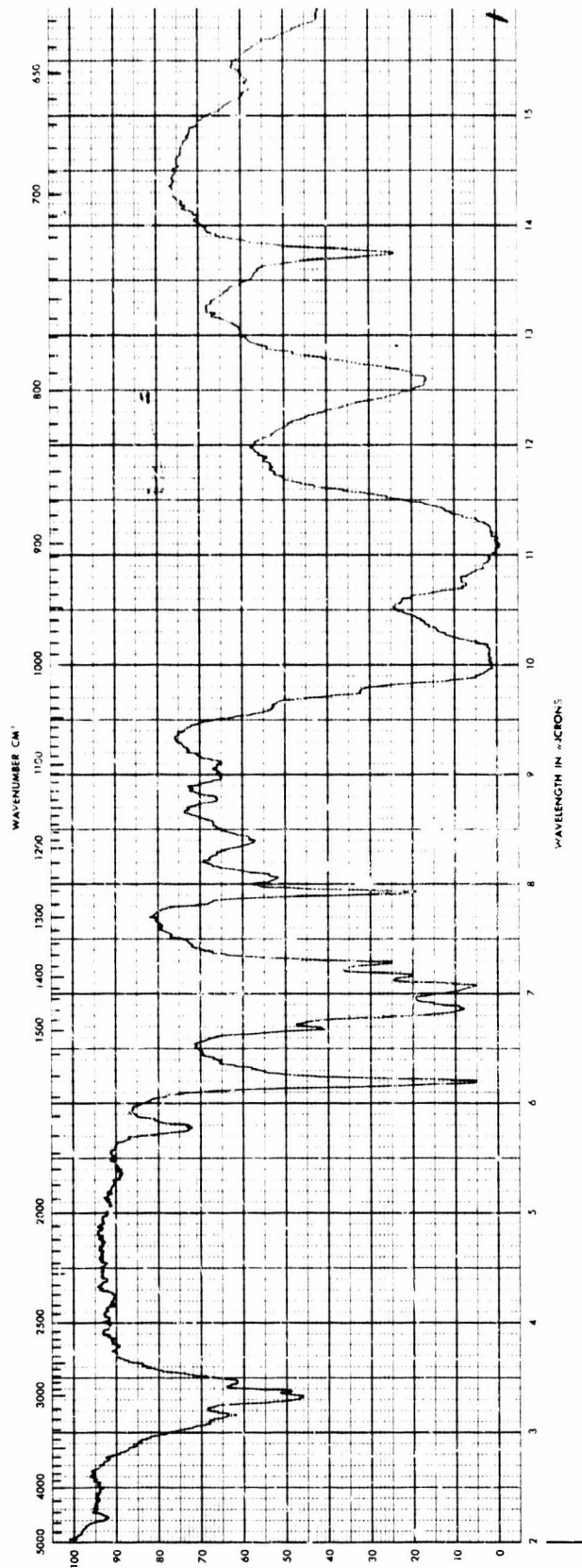
Infrared Spectrum of O-(2-difluoraminopropyl) Acetone Oxime

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Figure 1

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Infrared Spectrum of 2-Bromo-2,4,4-trinitropentane Difluoramine
Reaction Product

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Figure 2

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APPENDIX

HEAT OF FORMATION OF SAP BY ROTATING BOMB CALORIMETRY

by

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Sacramento, California

I. SUMMARY

The heat of formation of the compound FNH_3ClO_4 (unclassified name: substituted ammonium perchlorate or SAP) has been determined by combustion calorimetry using the rotating-bomb calorimeter, a platinum-lined combustion bomb (PT-1) and a reducing agent of arsenious oxide. Because of the extremely corrosive nature of the combustion products - HF , HNO_3 , Cl_2 and HCl - the platinum-lined bomb was used in place of the standard stainless steel unlined bomb. To obtain a chemically well defined final state of the chlorine, a reducing agent of arsenious oxide solution was placed in the bomb before each combustion to convert the Cl_2 to HCl .

The final derived heat of formation ($\Delta H_f \geq -67.6$ kcal/mole or -49.93 kcal/100 g) should be considered as a limiting value rather than an absolute quantity because of the assumption of 100% purity and extreme difficulties in handling. This value is in reasonable agreement with the preliminary heat of solution of -54.4 kcal/mole obtained by Fasolino (Reference 1) which leads to a derived heat of formation of -66.57 kcal/mole if the aqueous solution products are assumed to be $\text{ClO}_4^- + \text{F}^- + 1/3 \text{NH}_4^+ + 5/3 \text{H}^+ + 1/3 \text{N}_2(\text{g})$ (Reference 2).

Assuming equal heats of vaporization of NH_4ClO_4 and FNH_3ClO_4 and an N-H bond energy of 93.4 kcal/mole leads to a derived N-F bond energy of 57.1 kcal/mole.

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Heat of Formation of SAP by Rotating
Bomb Calorimetry (cont.)

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II. INTRODUCTION

The heat of formation of this compound is of interest not only as a high-energy solid propellant oxidizer, but also as one of the few known ionic compounds containing the FNH_3^+ radical. Of particular interest is a determination of the N-F bond energy for compounds of this general type.

The compound was first synthesized by Aerojet-General Corporation, Azusa, under contract to the Office of Naval Research (Reference 3). In preliminary work with a small sample of the original material, Fasolino (Reference 1) measured the heat of solution in water as -54.4 ± 1.4 kcal/mole, but did not have sufficient material to quantitatively identify the calorimeter reaction products.

In a later review of Fasolino's data, Coughlin (Reference 2) derived heat of formation values ranging from -66.57 kcal/mole to -20.49 kcal/mole, based on various assumed reaction products. Use of the mean value of -43 kcal/mole in a specific impulse calculation for a propellant consisting of 14% polybutadiene binder, 2% aluminum and 84% SAP leads to a theoretical I_s of 219 and an expected delivered I_s of 269. If the heat of formation of -66.57 kcal/mole is used (instead of -43) the theoretical I_s and expected I_s values are each reduced by about 9 units to 270 and 260, respectively.

The work reported here was also supported by the Office of Naval Research (in addition to a continuation of Fasolino's solution calorimetry work) as a means of arriving at an independent value for the heat of formation.

III. APPARATUS AND PROCEDURE

The calorimeter used in the measurements was an exact copy of the calorimeter designed by the U.S. Department of Interior, Bureau of Mines, Bartlesville, Oklahoma and described by Good et al. (Reference 4).

The procedure in general consisted of sealing the sample in polypropylene bags and burning in a platinum lined bomb in the presence of an excess of arsenious oxide aqueous solution. After completion of the sample combustion, the bomb was rotated to ensure complete reaction of the Cl_2 produced in the combustion with the As_2O_3 solution. The bomb combustion products were then analyzed for total acid, unburned carbon, unused As_2O_3 and platinum corrosion products.

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Heat of Formation of SAP by Rotating
Bomb Calorimetry (cont.)

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Before the actual measurements of the heat of combustion could be undertaken, a number of difficulties arose which first had to be overcome, aside from the corrosive nature of the combustion products. These were the extreme sensitivity of the sample to any trace of moisture, and chemical reactivity towards Mylar film which is usually used for sample combustion bags. Samples sealed in Mylar bags deteriorated quite rapidly when exposed to room air at 25% relative humidity and could not be stored more than a few hours even in the P_2O_5 dried nitrogen dry box. On the other hand, polypropylene film was found to be more inert to attack and impervious to moisture, at least for short exposure time with the sample, and it was used in place of Mylar film. The sample was found also to attack both glass and stainless steel handling utensils, even in the dry box, but polyethylene utensils were found to be sufficiently inert.

In attempting to find the best conditions for obtaining complete combustion, rather than burning explosively with charring of the polypropylene bag, a wide variety of experimental conditions were tried including the varying of the oxygen pressure; with and without the addition of auxiliary oil; use of thick and thin wall, deep and shallow crucibles; with and without a baffle constriction on the crucible. The best conditions found (least amount of unburned carbon) were with the sealed polypropylene bag in a deep, completely perforated, thin wall platinum crucible, cotton thread fuse, oxygen at 30 atm, and 20 cc of .36 N arsenious oxide solution added to the bomb. It was at these conditions that the three measurements listed in Table 1 were made, resulting in an average value for the measured combustion of -612.39 cal/g under bomb conditions (ΔE_B). Corrections to unit fugacity and a constant pressure process results in a standard heat of combustion (ΔH_c°) of -600.43 cal/g. The resultant derived heat of formation of this material based on the average heat of combustion and the theoretical composition is (ΔH_f) -508.00 cal/g or -68.82 kcal/mole ± 1.43 .

During shipment and handling, the sample (SAP) was kept in a covered nickel crucible inside a glass screw-cap jar containing a layer of P_2O_5 . The entire assembly was placed inside a dry nitrogen-filled dry box. The sample was exposed to this atmosphere only long enough to fill a polypropylene bag with the desired weight of sample and then returned to the P_2O_5 jar and sealed.

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Heat of Formation of SAP by Rotating
Bomb Calorimetry (cont.)

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The polypropylene bags were constructed from a sheet .50 mil (0.0125 mm) thick using the same method described by Good et al. for Mylar bags (5). After construction and weighing, the bag was placed inside the dry box for filling. Bags were left inside the dry box for periods up to 3 days, removed and weighed with no detectable gain or loss in weight.

The bags were filled using a polyethylene spatula and inserting a small polyethylene funnel into the neck of the bag to assure that no material adhered to the neck of the bag. After filling with the desired weight of sample, a special clamp was placed loosely around the neck of the bag and the bag pressed flat, to remove any excess nitrogen, and the clamp tightened. These were removed from the dry box, the neck was sealed, the clamp was removed, and the bag and contents were weighed. A weighed cotton-thread fuse was tied to the neck of the bag and this was rolled into a small ball and placed inside the perforated platinum crucible. A solution of standard arsenious oxide (20 cc) was added to the platinum-lined bomb and the bomb was sealed, flushed, and finally filled to 30 atm absolute pressure for all runs. The water was weighed into the calorimeter using a 10,000-g-capacity balance sensitive to 1 mg.

After completion of the combustion measurement, the bomb washings were titrated first with standard alkali for total acid content and then with standard iodine solution for unreacted As_2O_3 . The acid titration was conducted hot, in a Teflon dish, to the phenolphthalein end point in order to include HF as well as HCl and HNO_3 . The nitric acid correction was based on total acid minus the theoretical amounts of HCl and HF. Cl_2 formation was corrected for on the basis of the amount of As_2O_3 consumed; while the platinum corrosion correction was based on the average weight loss of the platinum crucible and support ring (9.5 mg per run).

IV. UNITS OF MEASUREMENT

All data reported are based on the 1961 atomic weights (Reference 6) and on a summary of fundamental constants listed by Rossini (Reference 7). For use in reducing weights in air to in vacuo, the following densities were used: SAP (ρ) 2.18 g/ml and for polypropylene (ρ) 0.907 g/ml. Standardization of the calorimetric

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Heat of Formation of SAP by Rotating
Bomb Calorimetry (cont.)

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system was performed by means of combustion with benzoic acid, Bureau of Standards, Standard Sample 39 i, and resulted in a mean energy equivalent of 4044.38 cal/deg with a precision uncertainty of ± 0.67 cal/deg or 0.015%. The values used for the heat of combustion of polypropylene and the cotton thread were: polypropylene (ΔE_c^0) - 11055.4 cal/g (Reference 8) and for cotton thread (ΔE_c^0) -4095.6 cal/g. To compute the value of the standard heat of formation of SAP, the following values were used for the standard heat of formation of water, hydrochloric acid, and hydrofluoric acid in kcal/mole: H_2O (Reference 1) -68.3173 (Reference 9); HCl (in 110 H_2O); and -39.669, and HF (in 110 H_2O), -76.342 (both Reference 10).

V. MATERIALS

The sample of SAP was prepared by Von Karman Center's Applied Chemistry Department and shipped for use here in a large nickel crucible with a nickel cover in a glass jar containing P_2O_5 . The sample was left in the crucible and P_2O_5 packing, and was placed in a dry box that was continually being purged with dry nitrogen.

The polypropylene film (.50 mil) was received through the courtesy of Dr. George Armstrong of the National Bureau of Standards, who also furnished the standard heat of combustion (ΔE_c^0) used for the corrections (Reference 8).

VI. ANALYSIS

Table 2 shows the results of analyses performed on the sample used in the calorimetric work before shipment from Azusa and after return of the unused portion. The uncertainty ranges shown opposite the individual analyses indicate the approximate range of variation obtained in duplicate analyses. It was not possible to obtain more precise analytical data by the usual combustion train technique because of the extremely explosive nature of the sample and because of additional uncertainties involved in the weighing and transfer of the analytical samples. The apparent value of carbon content (0.16 to 0.18%) is difficult to explain, however it is possible that gaseous HCl or HF bypassed the halogen trap during explosive burning and was subsequently picked up by the ascarite absorber. High values for hydrogen might be explained on the basis of moisture pickup during weighing and transfer. Decreasing values of N and F may indicate a real trend.

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Heat of Formation of SAP by Rotating
Bomb Calorimetry (cont.)

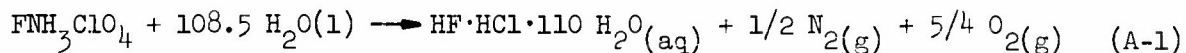
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Figure A-1 shows a comparison of the DTA traces for the same sample before shipment to Sacramento and after return to Azusa. Experience with many previous samples (Reference 3) has shown that the DTA trace is most sensitive to impurities or sample decomposition products. The pure material shows only a broad peak at 100-140°C and a smaller peak at about 280°C. Peaks at intermediate temperatures indicate the presence of impurities. As an example of the changes caused by exposure to moisture; the dotted line trace of Figure A-1 shows the effect of leaving a glass-capillary DTA sample in a covered Petri dish exposed overnight to room air.

In spite of the poor precision attained in the elemental analyses, some sample degradation is apparent from comparison of the December 1966 and March 1967 analyses. This is not surprising, in view of the extremely active nature of the sample and the number of handling steps which occurred between the initial and final analyses.

VII. MEASUREMENTS AND RESULTS

The results of the three heats of combustion measurements and corresponding derived heats of formation are summarized in chronological order in Table 1. The tabulated values of ΔE_B include all applicable corrections for ignition energy, nitric acid formation, Cl_2 formation, platinum corrosion and cotton thread and polypropylene bag combustions. The corrected combustion reaction corresponds to the equation:



A summary of the measured and derived data are shown in Table 3.

VIII. DISCUSSION OF RESULTS

From the time dependent trend in the measurements shown in Table 1, it appears that the sample may have deteriorated to a slight extent during handling and storage in the dry box between the first and third runs. Some evidence of sample deterioration prior to the start of measurements was also found in etching of the inside of the glass jar used for shipment; however, the total extent of decomposition could not be accurately determined from the results of the DTA and

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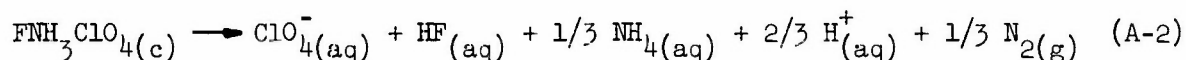
Heat of Formation of SAP by Rotating
Bomb Calorimetry (cont.)

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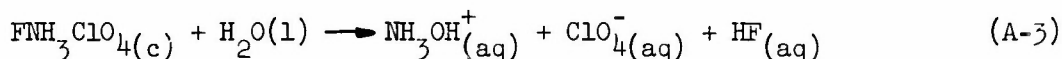
elemental analyses. Nevertheless, since the derived heats of formation are based on assuming 100% sample purity, the preferred value for the heat of formation is -67.64 kcal/mole based on the first run and should be considered as a limiting value rather than an absolute value.

The uncertainty as to the purity of the actual samples burned could have been resolved by a more complete analysis of the individual run combustion products, specifically by separate analytical determinations for NO_3^- , NO_2^- , F^- and Cl^- ions and for gaseous CO_2 . However, this work could not be performed within the allocated funding because of the amount of time required for the initial exploratory combustions.

Comparison of the present data with an earlier reported heat of solution measurement by Fasolino (Reference 1) (-54.4 \pm 1.4 kcal/mole) indicates possible agreement, depending upon final determination of the actual reaction occurring in the heat of solution reaction. The analytical data associated with this measurement were incomplete because of the small amount of sample originally available. Coughlin (Reference 2), in an analysis of Fasolino's data, derived heats of formation corresponding to several possible reactions, the most plausible of which were based on auto-oxidation of N:



This led to a derived value of -66.67 kcal/mole. The hydrolysis reaction

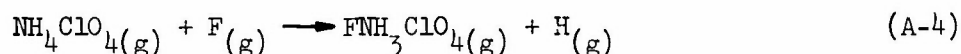


led to a derived value of -20.49 kcal/mole.

If Equation (A-2) is shown to be the actual heat of solution reaction, the two determinations will be in remarkably close agreement.

IX. BOND ENERGIES

The heat of the reaction,



was evaluated as +36.3 kcal/mole by assuming equal heats of vaporization of NH_4ClO_4 and FNH_3ClO_4 and utilizing the standard heats of formation of $\text{NH}_4\text{ClO}_4(\text{c})$, $\text{F}(\text{g})$, and $\text{H}(\text{g})$ from NBS Technical Note 270-1 (Reference 10). This data combined with

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Heat of Formation of SAP by Rotating Bomb Calorimetry (cont.)

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Pauling's (Reference 11) value of 93.4 kcal/mole for the N-H bond leads to a value of 57.1 for the N-F bond, which may be compared with Pauling's listed value of 64.5 for the N-F bond.

A further comparison may be made with the average value of the N-F bond in the gaseous molecule NF_3 (66.66) derived by comparison of the standard heats of formation of $\text{NH}_3(\text{g})$ and $\text{NF}_3(\text{g})$ (Reference 10).

X. RECOMMENDATIONS FOR FUTURE WORK

In a conversation with the Navy project monitor (Reference 12), it was learned that stable solutions of SAP in acetonitrile have been prepared. The use of such solutions could provide a number of distinct advantages in future calorimetric work:

- A. Sample purifications might be accomplished by crystallization from acetonitrile or by room temperature vacuum degassing to remove volatile impurities or decomposition products.
- B. Explosive combustion reactions could probably be eliminated by burning a series of SAP solutions. Separate measurements of heat of solution of SAP in acetonitrile would be required to derive the heat of formation of crystalline SAP.

In addition the SAP-acetonitrile solutions might have direct application as liquid or hybrid propellant ingredients.

Combustion calorimetry studies of SAP-acetonitrile solutions as well as further studies with crystalline SAP are recommended. In these studies greater emphasis should be placed on analysis of bomb combustion products as a means of improving the accuracy of the sample elemental analysis.

XI. ACKNOWLEDGMENT

Grateful acknowledgment is extended to J. R. Fischer and V. Grakauskas of the Applied Chemistry Department, Von Karman Center, Azusa, for sample preparation and analysis, and for helpful advice in sample handling techniques.

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TABLE 1

HEAT OF COMBUSTION AND FORMATION OF SAP

Sample Weight grams	$-\Delta E_B$ cal/g	$-\Delta H_f$ kcal/mole	d	d^2
1.4309	621.12	67.64	8.73	76.2129
1.3878	613.17	68.72	0.78	0.6084
1.4053	602.88	70.11	-9.51	90.4401
Av 1.3990	612.39	68.82	± 6.34	$(\Sigma d^2 = 167.2614)$

Precision Uncertainty = $2 \sqrt{\Sigma d^2 / n(n-1)} = 2 \sqrt{27.8769} = \pm 10.56$ or 1.72%

TABLE 2

SAP ANALYSIS

	12-1-66 Before	3-7-67 After	Theo.
C	0.16 ± 0.2	0.18 ± 0.2	0
H	2.7 ± 0.4	2.6 ± 0.4	2.23
N	9.6 ± 0.8	9.13 ± 0.8	10.34
F	13.8 ± 0.6	13.4 ± 0.6	14.02
Cl	-	-	26.17
O	-	-	47.24

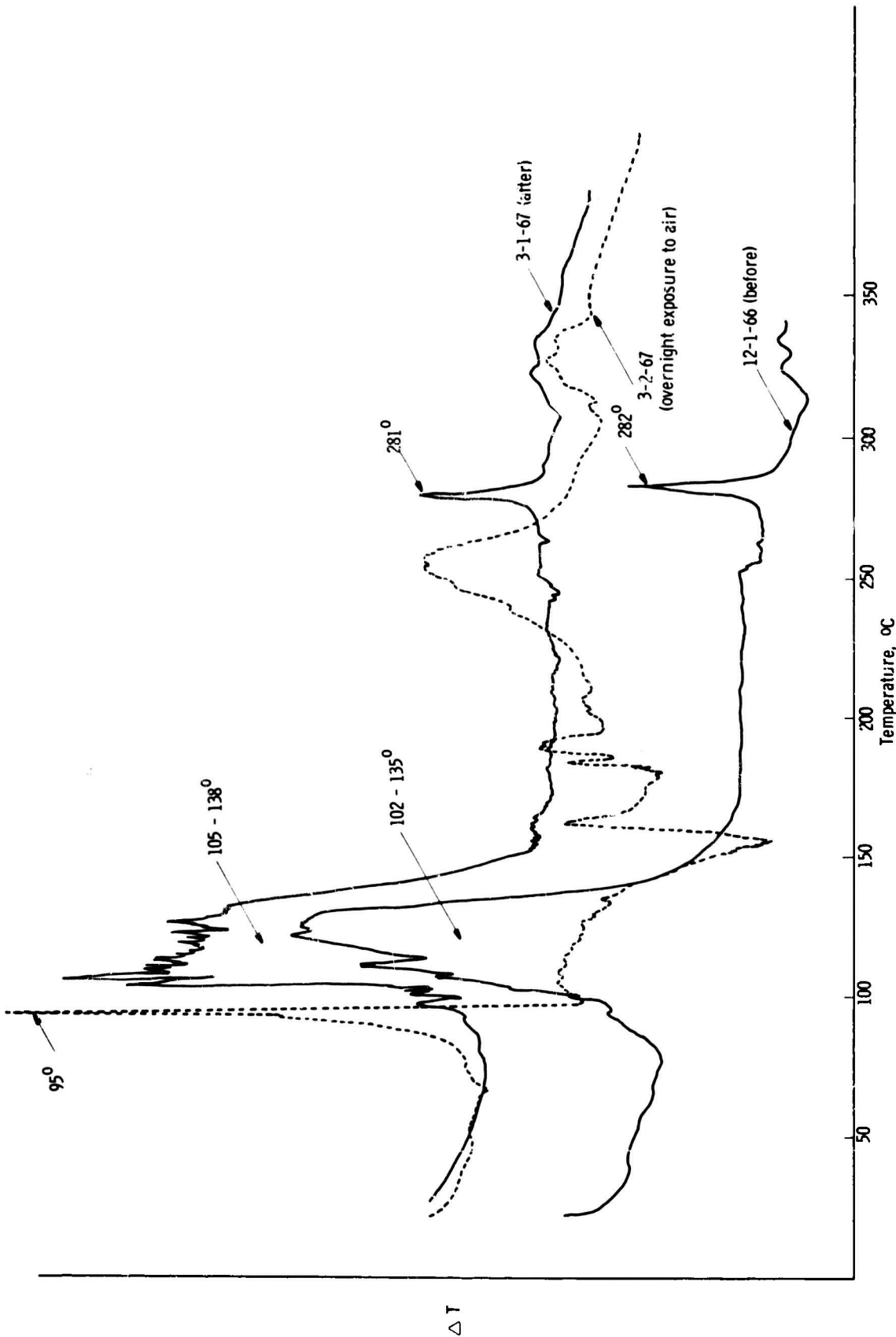
TABLE 3

SUMMATION OF DATA ON SAP

Empirical Formula	FH_2NClO_4
Molecular Weight	135.4796
Density (estimated)	2.18
ΔE_B (average), cal/g	-612.39 ± 10.56
Correction to Unit Fugacity	1.84
ΔE_C^O (constant vol), cal/g	-610.57
ΔnRT correction	10.14
ΔH_C^O (std. heat of comb.), cal/g	-600.43
ΔH_f (heat of formation), cal/g	-508.00 ± 10.56
ΔH_f (heat of formation), kcal/mole	-68.82 ± 1.43 (from average ΔE_B)
ΔH_f (heat of formation), kcal/mole	-67.64 (from Run No. 1)

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Tables 1, 2, and 3



Differential Thermal Analysis of SAP Sample
Used in Calorimetric Studies

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Security Classification

DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) Chemical Products Division Aerojet-General Corporation Azusa, California		2a. REPORT SECURITY CLASSIFICATION Confidential
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13. ABSTRACT The reaction of 2-phenylazo-2-nitropropane with difluoramine and fuming sulfuric acid gave 2-phenylazo-2-difluoraminopropane, benzene, acetone, 2,2-bis-(difluoramino)propane and O-(2-difluoraminopropyl)acetone oxime. The nitration of 2-phenylazo-2-difluoraminopropane has not yielded 2-nitro-2-difluoraminopropane, although 2-phenylazo-2-nitropropane gave 2,2-dinitropropane. No product of interest resulted from the reactions of difluoramine with ethyl nitrodiazacetate, ethyl 2-butylnitronate, 1-diazo-2-heptanone, 2-nitropropene, diphenyliodinium tosylate, and 1-iodo-1-nitrocyclohexane. A new NF compound was found in the reaction of 1-nitro-1-nitrosocyclohexane with difluoramine and 100% sulfuric acid. The reaction of 2-bromo-2,4,4-trinitropentane with difluoramine and fuming sulfuric acid resulted in extensive replacement of nitro groups. The reaction of 3,3-bis(difluoramino)pentane with fluosulfonic acid gave 3-pentanone and difluoramine. Fluoroammonium perchlorate underwent no decomposition in 4 months at ambient temperature in a Teflon container. An approximate value of the heat of formation of SAP, -67.6 kcal/mole, was determined by rotating bomb calorimetry.		

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